Thin transparent conducting films based on core-shell latexes

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5 Latex film formation at room temperature

In the chapters 3 and 4 it has been shown that transparent films can be formed from PBMA latexes encapsulated with a polypyrrole shell. The rate of film formation strongly depends on the thickness of the polypyrrole shell and on the temperature at which the film is formed. Since film formation at high temperatures has a number of disadvantages, such as loss of conductivity and limitation of substrate composition and size, the possibility to form transparent films from a 1 wt% PPy-encapsulated PBMA latex at room temperature has been investigated in this chapter.

Three different routes to form such films have been investigated. It has been found that it is possible to obtain transparent films from blends of encapsulated latexes and film-forming latexes, but the quality of the films is rather low. The homogeneity of the films is not very good, resulting in "sandy-like" structures in the films. This is attributed to colloidal instability of the latex.

A second method to form films at room temperature is by using low-T_g acrylic latex particles or PBMA latex particles with a low-T_g shell as the core particles. Depending on the T_g of the polymer and the thickness of the acrylic shell it is possible to form films based on these latexes, but these films proved to be electrically insulating or inhomogeneous.

A third method is to employ so-called coalescing aids. It has been found that it is indeed possible to obtain homogeneous transparent films from 1 wt% PPy-encapsulated PBMA latexes with a proper choice of the coalescing aid. The best results were obtained with Dowanol EPH, which is an ethylene glycol phenyl ether. Films formed with this coalescing aid can have a transparency of well over 90%. The film transparency is found to depend on the concentration of coalescing aid, the film thickness, and on the relative humidity at which the film is formed.

5.1 Introduction

In the previous chapters it has been shown that conducting latex particles with an acrylic core and an ICP shell can be prepared and that transparent films can be obtained from such encapsulated latexes by heating. It was shown that the ICP shell forms a strong barrier against film formation and high temperatures and/or long annealing times are necessary to obtain transparent and mechanically strong films. Such a heat treatment has a number of disadvantages. It limits the practical applicability of the conducting film, because severe prerequisites are set for the substrate on which the coating is applied. The size and shape of the sample on which the film is applied are limited because it has to be heated in an oven. Finally, it is well known that ICPs often suffer from loss of conductivity with time, especially at elevated temperatures [1]. Although polypyrrole is one of the most stable ICPs with respect to its conductivity, it is advisable to prevent elevated temperatures as much as possible.

One can think of several approaches to forming transparent films from encapsulated latex particles without the necessity of a heat treatment. First, it is possible to blend a film-forming latex with the encapsulated latex. Upon evaporation of the water, the film-forming latex can deform and fill the voids between the encapsulated latex particles, thus providing a matrix that gives the film mechanical strength and prevents the scattering of light by voids. Second, one can use a core latex from an acrylic polymer with a lower T_g than PBMA or use a composite particle with a PBMA core and a low T_g shell in the in-situ polymerization of the ICP. Upon evaporation of the water, the acrylic core latex will have a lower resistance against deformation and can deform resulting in a transparent and mechanically rigid film. A third method to obtain film formation of the encapsulated latexes at room temperature is to employ so-called coalescing aids or coalescents. These are low molecular weight liquid compounds that are added to the aqueous latex and temporarily lower the T_g of the latex polymer. After film formation of the latex, the coalescing aid evaporates and the latex polymer regains its original glass transition temperature.
All three methods have been investigated for their usefulness in the preparation of transparent films based on PPy-encapsulated latexes.

5.2 Film formation of blends with low-T_g latexes

In recent years more and more research effort is directed to the combination of different polymers in order to prepare materials which combine the desirable properties of the individual components and have a good overall performance. One of these areas is the preparation of polymeric films from blends of latexes [2, 3]. It has been shown that when a film-forming latex is blended with a non-film-forming latex, a transparent film is formed if the non-film-forming particles are uniformly distributed in the polymer matrix generated from the deformed soft particles. However, if the hard latex particles form clusters, the resulting film is turbid [2]. Various factors, such as the size ratio between the two types of particles, the presence of surfactants, and annealing of the films after drying, influence the uniformity of the particle packing that is required for transparent films. If the size of the latex particles is comparable, transparent films are formed if the soft particle volume fraction exceeds ~0.5 [4]. At lower volume fractions voids are still present in the film. These voids can scatter light and reduce the film transparency. Which of the two polymers in the latex blend forms the continuous matrix does not only depend on the volume ratio between both latexes, but also on the ratio of their particle sizes [5]. When the differences in particle size are significant (d_{hard}/d_{soft} = 4–10) a continuous matrix of the soft particles can be formed with only 30 vol% of the soft particles if the packing of the particles is good [5, 6, 7].

To the best of our knowledge, there is only one report of the preparation of latex blend films with ICPs. Cooper et al. [8] have prepared blends of a PMMA/PBA latex with preformed PANI and PPy particles. The diameter of the acrylic latex was about 160 nm and the polypyrrole particles were rather polydisperse with most particle diameters in the range 100–150 nm. From these water-based systems, films could be prepared with a conductivity of about 10^{-2} S/cm with only about 5 wt% PANI or about 20 wt% PPy. The difference in the percolation threshold is attributed to the difference in shape of the ICP particles; the PANI particles are needle-shaped and the PPy particles have a more globular appearance. Cooper et al. reported that the films essentially retain the mechanically properties of PMMA/PBA films up to ICP particle concentrations of ~20 wt%. At higher concentrations the films become brittle and easily torn [**Error! Bookmark not defined.**].

When we tried to prepare blend films based upon ICP-encapsulated latexes and film-forming latexes, various difficulties were encountered. The main problem is the colloidal stability of both latexes in the mixture and therefore

the uniformity of the distribution of the particles in the film. Especially if small, low-T_g particles are employed, the colloidal stability is usually low. This might be due to the large increase in latex surface area available to the stabilizer molecule. This can result in desorption of stabilizer molecules from the encapsulated latex particles and thus in destabilization. The use of small, low-T_g particles is advantageous over using larger particles because it reduces the size of the voids between the latex particles in the film upon evaporation of the water. This reduces the minimum film formation temperature and thus the temperature at which transparent films are formed [9]. The stability can be improved by the addition of extra stabilizers like SDS, but this has the disadvantages that it may decrease the final film transparency and that the hydrophilicity of the film will be increased.
We have been able to prepare transparent and conducting films from blends of encapsulated latexes with low-T_g latexes. However, none of these films was homogeneous, resulting in "sandy-like" structures in all latex films. This limits the transparency and the mechanical strength of the film. Therefore, other methods to obtain homogeneous films have been developed.

5.3 Film formation of encapsulated latexes with a low-T_g inner shell

A second approach to obtaining film formation at room temperature is the use of core latex particles with a lower T_g than PBMA. Such particles can either be homogeneous, i.e. have the same composition throughout the particle, or have a core–shell structure in which the low-T_g polymer is situated at the outside of the PBMA latex. In this study such core–shell latexes have been used. A schematic presentation of the film formation of such a latex after encapsulation with polypyrrole is given in Figure 5.1.

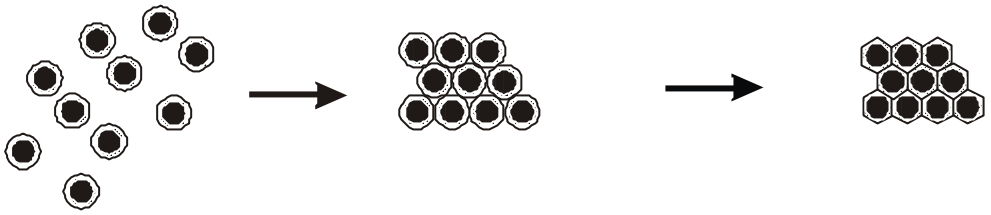

Figure 5.1 Schematic presentation of the film formation process of an encapsulated latex with a low-T_g inner shell.

In the third stage of the film formation process, the PBMA core keeps its spherical structure. If the thickness of the low-T_g shell is high enough and the T_g of this polymer is low enough, the soft acrylic shell will deform and fill the voids between the latex particles. In our case the shell thickness and the T_g of the soft acrylic shell are even more important, since the encapsulation by polypyrrole gives an extra resistance against particle deformation, as can be seen in the atomic force microscopy images shown in Figure 5.2.

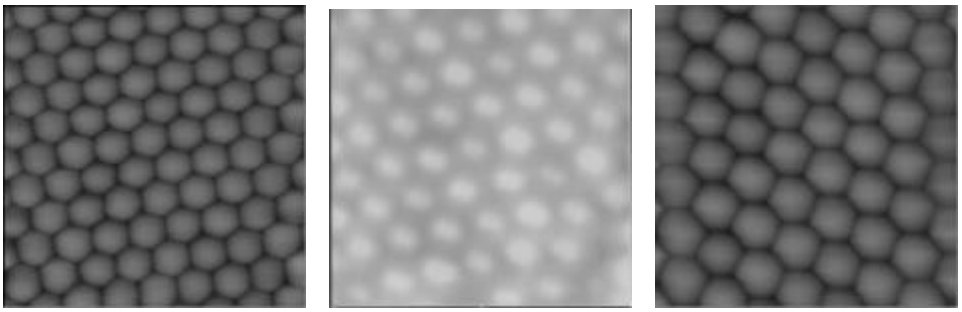

Figure 5.2 AFM images of samples dried at room temperature of the PBMA core latex (left), the PBMA core latex with a 50 nm shell of a PBMA-PBA copolymer with a T_g of –15 °C (middle), and of the same latex but after encapsulation with 1 wt% PPy (right). The size of all three images is 5×5 µm.

The images in Figure 5.2 were taken on thick latex films that were dried at room temperature. In the left-hand figure, the particles are stacked nicely in

a lattice and the boundaries between the individual particles are clearly visible. This is as expected, since the particles were dried at room temperature, so below the T_g of the latex polymer. In the picture in the middle, the size of the spherical particles is the same as in the left-hand figure, but they appear separated. This is due to the film formation of the low-T_g shell polymer that was polymerized around the PBMA core particles. The appearance of this sample is transparent, whereas the dried PBMA latex is white due to the scattering of light by the voids in the sample. Polymerization of a polypyrrole shell of about 1 nm around the latex particles with the low-T_g shell hinders the film formation of the particles, as can be seen in the right-hand figure. Here the boundaries are clearly visible again. Since these samples are rather thick, the appearance of the PPy-encapsulated film was very dark. That film formation had indeed occurred in this case could be concluded from the mechanical strength of the film.

In general, core–shell particles with a low-T_g shell are used in order to get a desired combination of properties, i.e. a good combination of the rate of film formation and the hardness of the resulting film. In this study, such core–shell particles are used since it offers the possibility to use the same PBMA core latex and polymerize low-T_g shells with different properties (composition and nature of the monomer) around this core latex. This enables the comparison of the influence of the different shells independent of factors like the exact size and composition of the core latex.
It was found that transparent latex films can be formed from PPy-encapsulated latex particles with a low-T_g inner shell and a diameter of about 800 nm if the T_g of the shell-polymer is below –15 °C and the thickness of the shell is at least 50 nm. The colloidal stability of these latexes, however, is found to be worse than that of encapsulated latexes with a pure PBMA core. The reason for this lower colloidal stability is not understood. A possible explanation could be a lower binding efficiency between the HEC thickener and the acrylic latex during the in-situ polymerization of the pyrrole, but the reason for such a lower binding energy is not clear. The lower colloidal stability of the latex, however, has a negative influence on the quality of the films. Via incorporation of acrylic acid groups in the shell it is possible to prepare latexes that are colloidally stable even during the in-situ polymerization of pyrrole. However, as has already been said in chapter 2, such latexes proved to be non-conducting and were therefore not used further in this study. Since films with much better optical properties could be obtained at room temperature using other methods, the colloidal stabilization of PPy-encapsulated latexes with a low-

T_g inner shell has not been investigated in more detail. However, since this method has proven to be applicable and since it really enables the formation of transparent films at room temperature without extra additives, it deserves further investigation.

5.4 Film formation of encapsulated latexes with coalescing aids

In commercial latexes usually small amounts of volatile organic solvents are present. These organics are called coalescing aids, coalescents or filming aids and they facilitate the deformation of the latex particles and the chain interdiffusion between different latex particles upon evaporation of the aqueous phase. After the film has been applied, the coalescing aid evaporates from the film, thus restoring the original latex polymer properties.
The mode of action of coalescing aids in latexes is rather complicated. From experiments with bulk polymers it is known that a coalescing aid can lower the T_g of the polymer [10]. Since the elastic modulus of a polymer decreases by several orders of magnitude as the temperature is raised above its T_g, a coalescing aid promotes the ease of particle deformation [11] and chain interpenetration [12]. In an aqueous latex the situation is more complicated since also other factors like the partitioning of the coalescing aid between the water phase and the polymer phase play a role. This partitioning influences the concentration of coalescing aid in the polymer phase and in the water phase. The presence of coalescing aids in the water phase may retard the evaporation of water in the very last stage of the drying of the latex by reducing the partial pressure of water [13]. Since evaporation of water is an endothermic process, this will increase the temperature of the latex during coalescence [14] and it results in a decrease of the air void formation in the film [11].
There are many different coalescing aids commercially available, all with their specific affinity for different polymers, water solubility and evaporation rate. In this project six different coalescing aids that are often employed with acrylic latexes are investigated for their influence on the film formation of PBMA latex particles encapsulated with 1 wt% PPy. The main properties of the coalescing aids are given in Table 5.1.

Table 5.1 Main properties of the coalescing aids [15].

Trade name	Chemical name	Evaporation rate[1]	Solubility in water (wt%, 20°C)
Dowanol EB	Ethylene glycol *n*-butyl ether	0.06	8
Dowanol DPM	Dipropylene glycol methyl ether	0.035	8
Dowanol PnB	Propylene glycol *n*-butyl ether	0.093	5.5
Texanol	2,2,4-trimethyl 1,3-pentanediol monoisobutyrate	0.002	insoluble
Vestinol AH	Dioctyl phthalate		insoluble
Dowanol EPH	Ethylene glycol phenyl ether	0.001	2.5

[1] The evaporation rates are compared to *n*-butyl acetate = 1

It was observed that the wetting of the glass slide by the different latexes is very different, ranging from very good for the sample with Dowanol EPH to rather poor for the sample with Dowanol EB and Dowanol DPM. A poor wetting results in inhomogeneous drying of the film and thus in an inhomogeneous film. In the paint industry, such drying effects are often solved by a modification of the paint viscosity via rheology modifiers or thickeners. A second mode of action of such a thickener is that it can change the properties of the aqueous phase and make it better wetting the substrate. Therefore, latex films have been prepared with a hydrophobic polyurethane thickener that is often used in latex systems, SER AD FX 1100. The amount of thickener used is about 5 wt% relative to the total (wet) latex. The amount of coalescing aid relative to the solid latex polymer is 20 wt%. The thickness of the wet films is approximately 15 µm. The final transparencies of the thus prepared latex films are plotted in Figure 5.3.

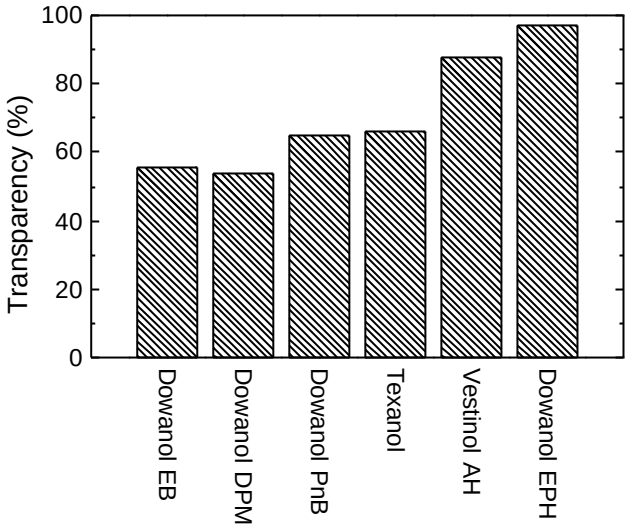

Figure 5.3 Transparencies of films prepared with different coalescing aids from a 1 wt% PPy-encapsulated PBMA latex at room temperature with 5 wt% SER AD FX 1100; Relative Humidity (RH) = 94%; wet film thickness = 15 µm; [coalescing aid] = 20 wt%; solid content = 14.6%.

As can be seen from Figure 5.3, large differences in film transparency are found with the different coalescing aids and, more important, it is possible to obtain transparent films from the encapsulated latexes at room temperature. In Chapter 6 is shown that these transparent films can possess a resistance of less than 100 kO/?, so it is possible to prepare transparent, antistatic films at room temperature.
The performance of Dowanol EPH as a coalescing aid is superior in comparison with the other coalescing aids. As has been said in the beginning of this paragraph, the mode of action of coalescing aids is very complicated and therefore it is not possible to relate the coalescing strength directly to a certain property. In this case, however, a possible explanation for the superior performance of Dowanol EPH could be its chemical structure in combination with its partition in the water phase and the latex particle. As has been shown in the previous chapters, the polypyrrole shell forms the main resistance against deformation of the encapsulated latex particles. One of the characteristics of polypyrrole is its conjugated ring-structure; a structure that is also present in the two coalescing aids that give

the best results, Dowanol EPH and Vestinol AH. Therefore, some affinity between the polypyrrole and these coalescing aids can be expected. The difference in performance of Vestinol AH and Dowanol EPH is possibly due to the difference of the partition of the coalescing aid inside the latex particles. The water solubility of Dowanol EPH is much larger than that of Vestinol AH. Upon evaporation of the water, the coalescing aid that was present in the water phase will be forced into the latex particles, because its evaporation rate is lower than that of water. Therefore it can be expected that immediately after the evaporation of the water, in the case of Dowanol EPH more coalescing aid will be present at the outside of the particle than in the case of Vestinol AH. The main resistance against deformation, the polypyrrole shell, is located only at the surface of the latex particle. Since more Dowanol EPH will be located near this shell, this might be an explanation for the better performance of this coalescing aid.
Since the samples with Dowanol EPH as the coalescing aid give the best results, this coalescent is selected for further experiments.

The viscosity of the aqueous latexes can be adjusted not only by the addition of thickeners, but also by the concentration of the latex in the water. Therefore, part of the water phase is evaporated prior to the addition of the coalescing aid, until the solid content of the latex is about 28 %. Such a solid content proved to be high enough for the preparation of homogeneous films from the 1 wt% PPy-encapsulated latexes with Dowanol EPH as the coalescing aid. The concentration process does not have a negative influence on the colloidal stability of the latex, neither immediately, nor in the long term. This concentrated encapsulated latex, without any additional thickener, is used for further experiments.

So far, the concentration of the coalescing aids has been kept constant at 20 wt% relative to the solid polymer. Since coalescing aids are organic liquids, they evaporate from the film. The use of so-called volatile organic compounds in paints is reduced as much as possible since such compounds are suspected of causing the Organic Psycho Syndrome (OPS) and the greenhouse effect. Therefore, the influence of the concentration of Dowanol EPH on the final film transparency is investigated.

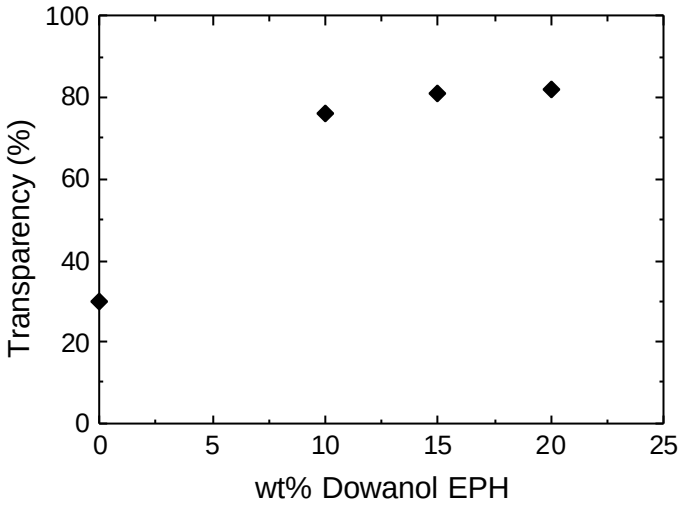

Figure 5.4 Transparencies of films prepared with different concentrations of Dowanol EPH from a 1 wt% PPy-encapsulated PBMA latex at room temperature; RH = 94%; wet film thickness = 15 µm; solid content = 28.4%.

A relation between the concentration of Dowanol EPH and the film transparency is found, as can be seen in Figure 5.4. The final film transparency increases from about 75% for the sample with 10 wt% coalescent, to well over 80% for the sample with 20 wt% Dowanol EPH. Without any coalescing aid, the transparency of such a film is only about 30%. Since there is only a very small increase in film transparency upon increasing the coalescent concentration from 15 wt% to 20 wt%, it is clear that a concentration of 20 wt% Dowanol EPH is near the optimum for this latex [11].

The fact that the final transparency of the film that is prepared with 20 wt% coalescent is clearly lower in Figure 5.4 than it was in Figure 5.3 can have two origins. First, because the latex that was used for Figure 5.4 was more concentrated and the wet film thickness was kept constant, the thickness of that film will be larger. Of course, this will increase the amount of absorbed and scattered light, even if the number and size of voids per unit film volume remains unchanged. Second, since the amount of water is lower in the concentrated latex, the film will be dry in a shorter period of time. This

limits the time that the particles can move in the liquid and may therefore result in a poorer stacking of the particles in the film and thus in an increase in number and size of the voids.

The influence of the rate of water evaporation on the film transparency was investigated by forming the film at different relative humidity (RH). At a higher RH, the driving force for water evaporation is lower, leading to an increase in the time interval that the particles can move in the water phase. This decrease in evaporation rate indeed has a positive influence on the film transparency, as can be seen in Figure 5.5.

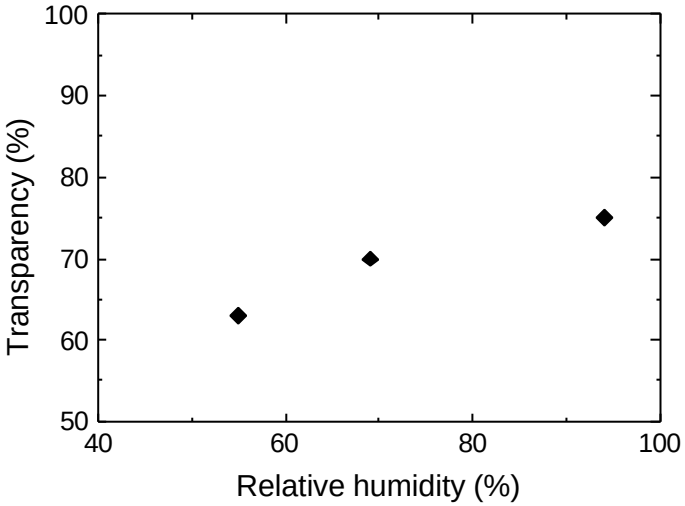

Figure 5.5 Transparencies of films prepared at different relative humidities from a 1 wt% PPy-encapsulated PBMA latex with 10 wt% Dowanol EPH at room temperature; wet film thickness = 15 µm; solid content = 28.4%.

The transparency of the film clearly depends on the relative humidity at which the film is formed. A difference in relative humidity results in a difference in the time that liquid water is present in the film, which ranges from about 7 minutes for the film at 55% RH to about 50 minutes for the film dried at 94% RH. The difference in film transparency can have two origins. First, as has been indicated already, a faster drying limits the time available for the particles to stack in a perfect lattice. Therefore, more and

larger voids will be present in the film formed at low RH. Second, water evaporation is an endothermic process, thus the evaporation of water will decrease the actual temperature of the latex during coalescence. Hence, the shear modulus of a latex drying at low RH will be higher than the shear modulus of the same latex drying at a higher RH. The deformation is facilitated in the latter case, resulting in a film with smaller voids and thus a higher transparency [14].

5.5 Conclusions

Three different methods to form transparent films from acrylic latex particles encapsulated with 1 wt% PPy at room temperature have been investigated. It has been found that it is possible to obtain transparent films from acrylic latexes with a low-T_g inner shell and from blends of a PPy-encapsulated latex with a film-forming latex. However, the optical quality of such films is rather low. This has been attributed to colloidal instability of the latex, which causes inhomogeneity in the film and therefore limits the film transparency. Much better results were obtained with films formed with coalescing aids. It has been shown that it is possible to form >90% transparent films with the proper combination of type of coalescent, concentration of coalescent, and drying conditions.

The best results have been obtained with Dowanol EPH, which is an ethylene glycol phenyl ether. The superior coalescing power of this coalescing aid might be attributed to the presence of a conjugated ring in its structure in combination with an intermediate partitioning between the water and polymer phase. It has been shown that another coalescent, with a conjugated ring but with a much lower water solubility, is only slightly less effective, while other coalescents, without the conjugated ring, are much less effective.

The transparency of a film that is formed with Dowanol EPH depends on many different variables, such as the concentration of the coalescing aid, the thickness of the film, and the relative humidity at which the film is formed. It has been found that a concentration of about 20 wt% Dowanol EPH relative to the solid latex content is the optimum for a 800 nm diameter PBMA latex encapsulated with 1 wt% PPy at a solid content of approximately 28.4%. At a lower RH, the evaporation of the water phase is faster. This reduces the time that the latex particles can move freely through

the film in order to get the optimum lattice-like particle stacking and it also reduces the actual temperature of the film. This results in an increase of the size of the voids in the film and thus in a reduction of the film transparency.

5.6 Experimental

Latex synthesis

The core PBMA latex was synthesized in an emulsifier-free batch synthesis according to the procedure described in chapter 3. The diameter of the latex that was used throughout this chapter was determined using a Brookhaven Instruments BI-DCP Particle Size Analyzer. The diameter of the particles was about 800 nm unless indicated otherwise.

Two different routes have been employed for the formation of the latex particles with a low-T_g inner shell. In the first method, first a PBMA latex is synthesized according to the emulsifier-free batch method and this latex is subsequently dialyzed in order to remove excess initiator and salt. Next, oxygen is removed from the latex again by bubbling N_2 through the mixture followed by the formation of the low-T_g shell via a semi-continuous polymerization of the shell polymer. In the second method, the core latex was polymerized according to the same procedure. The shell, however, was polymerized directly on this core in a semi-continuous polymerization, so no intermediate dialysis was performed. In the latter procedure, “living” radicals can be present on the latex surface and therefore the acrylic shell chains may be chemically linked to the core. An advantage of the first method, however, is a better control of the monomer-to-oxidant ratio in the shell polymerization. Furthermore, if one wants to compare the influence of different shell compositions, it is possible to start with exactly the same core latex thus ruling out the influence of this core on differences in, for example, film formation. No relation between the mode of synthesis of these latexes and their film formation behavior after encapsulation has been observed.

Low-T_g latex particles that were used in blends were synthesized according to the same procedure as the PBMA core particles. The size of the latex particles was controlled by the monomer-to-oxidant ratio.

The polypyrrole encapsulation protocol has been kept constant throughout the experiments described in this chapter. This protocol has been given in chapter 3.

Film transparency measurements

A film-drying chamber was used in which a latex dispersion can be dried in well-defined conditions. Dr. J. Laven and M. Visscher of the Technical University of Eindhoven have developed this film-drying chamber and kindly placed it at the disposal for these experiments.

In order to measure the film transparency, a sample of the aqueous latex is applied on a glass slide using a floating knife and inserted in a double-walled glass chamber. Temperature-controlled water is circulated through the wall, keeping the temperature inside the chamber at 23 ± 1 °C. With the aid of electrolyte solutions the relative humidity in the chamber is controlled. A saturated $MgNO_3$ solution results in a relative humidity of 55%, KBr is used for the experiments at 69%, and experiments at 94% RH were done in the presence of pure liquid water. The progress of film formation is monitored optically using a low-energy laser (633 nm) and a photodiode. First the correction factor C is determined as the photodiode signal measured when a non-coated glass slide is placed between the laser and the photodiode. The transparency of the latex film is determined using the same geometry but with the glass slide coated with the latex according to the procedure described above. The transparency of the film is calculated from the photodiode signal using the correction factor. Transparency values reported in this chapter are the film transparencies 200 minutes after application of the film. These are all dry-film transparencies, liquid water having evaporated from all films in less than 60 minutes.

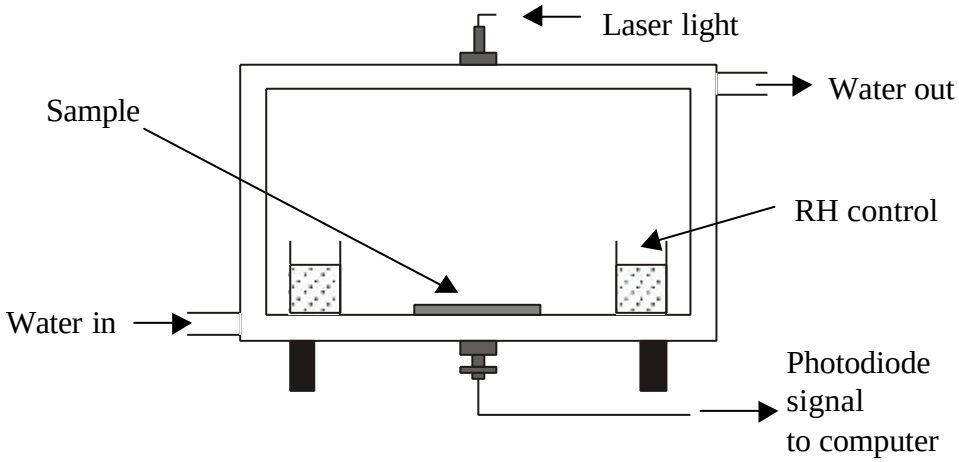

Figure 5.6 The film-drying chamber and the optical detection system.

Additives

The coalescing aids Dowanol EB, Dowanol DPM, Dowanol PnB, and Dowanol EPH were kindly donated by Dow. Texanol was kindly donated by Eastman Chemical Company, and Vestinol AH was kindly donated by Hüls AG. All coalescing aids were used as received. The latexes with coalescent were allowed to stabilize and reach equilibrium by stirring them gently for at least one week.

The thickener SER AD FX 1100 was kindly donated by Servo Chemicals. The thickener was used as received and added to the latex as a 3.85 wt% solution in water. The latexes with thickener were allowed to stabilize and reach equilibrium by stirring them gently overnight.

5.7 References

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